PROCESS FOR ELECTROLYTIC PRODUCTION OF ALUMINUM

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CONTRACTUAL ORIGIN OF INVENTION

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Chicago, representing Argonne National Laboratory.

BACKGROUND OF THE INVENTION

10   **1. Field of the Invention**

This invention relates to an electrolyte and a method for producing aluminum at

lower temperatures, and, more specifically, this invention relates to an electrolyte that

enables a method for producing aluminum at lower temperatures using a myriad of

electrodes, including inert anodes and wettable cathodes.

15   **2. Background of the Invention**

Primary aluminum is produced by the electrolysis of alumina in a cell (or pot)

containing a molten fluoride salt based on the AlF_3-NaF system. During electrolysis,

carbon dioxide gas forms at the anode and escapes from the cell, while liquid aluminum

metal forms at the cathode at the bottom of the cell. The electrolytic process (called the

Hall-Héroult process) operates at temperatures in excess of 900°C. Such high temperatures are detrimental for a number of reasons, including deterioration of cell components.

Another drawback to typical aluminum production processes is the use of consumable carbon anode materials. The gradual consumption of the carbon anodes, due to reaction of the carbon with oxygen forming carbon dioxide gas bubbles at the anode surface, necessitates constant repositioning of the remaining anode with the cathode to maintain an optimal anode-to-cathode distance. Ultimately, the anodes must be replaced. Also, the manufacture and use of carbon anodes contributes to the production of greenhouse gases such as carbon dioxide and perfluorocarbons (PFCs).

The aluminum community has long-searched for a so-called inert anode (one that is not consumed by the electrolysis process) for use in aluminum production cells to replace consumable carbon anodes. This research has spanned several decades. All of the so-called inert anode materials characterized to date have had various shortcomings with respect to attributes needed for commercial success. Anodes made of ceramic or cermet materials cause some practical engineering problems, such as poor thermal shock resistance, electrical connection, operational challenges and scalability etc. Anodes made of metal have the potential advantage of improved electrical and mechanical performance over cermet or ceramic materials. However, work on metal anodes at high temperatures (i.e., between 900°C and 1000°C) has had only limited success.

Low temperature electrolytes, those that remain liquid below 800°C, can increase the utility of inert anodes. Recent work in this area has mainly focused on the sodium fluoride (NaF) – aluminum fluoride (AlF_3)-based electrolyte system, i.e. so called low bath ratio (NaF/AlF_3) melts. Due to a relatively low solubility of alumina (Al_2O_3) in these low-temperature (around 750°C) electrolytes, a slurry-cell concept was proposed to keep solid alumina in suspension during electrolysis, allowing the alumina activity in the electrolyte to remain high during electrolysis. However, slurry-cell operation causes operational difficulties and problems with metal collection, as well as the fact that very strict requirements on cell design are needed to maintain the alumina in suspension.

Another drawback to typical aluminum production processes is the need to maintain a sufficient molten aluminum metal pool at the bottom of the cell. Significant operation difficulties occur when the carbon blocks on the cell bottom are exposed to the molten salt electrolyte bath. Since molten aluminum does not wet carbon, a significant quantity of aluminum is required to totally cover the cell bottom. The presence of this deep aluminum pool leads to process inefficiencies due to fluctuations at the bath-aluminum interface resulting from magnetic fields generated in the metal pool during electrolysis. These fluctuations are minimized with the use of so-called wetted cathodes, i.e., cathode substrate materials that are wet by molten aluminum.

Still another drawback to typical aluminum production is the large dimensions or "footprint" of the typical alumina electrolytic cell. This is due to the horizontal alignment of the electrodes, necessitated by the lack of suitable inert anodes and wetted cathodes required to maintain a stable anode-to-cathode distance in cells with vertically aligned electrodes.

A need exists in the art for an electrolytic method for aluminum production that operates in low-temperature electrolytes, i.e., one with an operating temperature less than $800^{\circ}C$. The method should eliminate the need for consumable carbon anodes and allow for the use of inert anodes, wetted cathodes, and/or bi-polar electrodes in horizontal, vertical, or other arrangement. The method should also provide for a constant distance between anode and cathode during the electrolysis of alumina to provide an electrically stable electrolysis environment. In addition, the method should provide an electrolyte which is entirely liquid at the operating temperature.

SUMMARY OF INVENTION

An object of the present invention is to provide a method of alumina electrolysis that overcomes many of the disadvantages of the prior art.

Another object of the present invention is to electrolyze alumina to aluminum at temperatures lower than $800^{\circ}C$. A feature of the invention is an electrolyte salt bath based on a mixture of aluminum fluoride (AlF_3) – potassium fluoride (KF) containing alumina (Al_2O_3) for aluminum production by electrolysis. An advantage of this invention is that it allows for the electrolytic production of aluminum at lower temperatures, and thus lowers costs including capital, operational, and environmental costs.

Still another object of the present invention is to provide an electrolyte whereby the electrolyte is stable during electrolysis operations. A feature of the invention is an electrolyte which has a relatively low vapor pressure (less than 10 millibar) in the process range temperature of between 660^{0}C and 1000^{0}C. An advantage of this

5   feature is that the concentrations of the electrolyte's components remain relatively constant during electrolysis.

Yet another object of the present invention is to provide an electrolyte which maintains a liquid phase during electrolysis operations. A feature of the invention is an electrolyte which has higher alumina solubility than in currently used low-temperature

10   electrolytes. An advantage of this feature is that cell design and operation requirements become more flexible.

Still another object of the present invention is to provide a method whereby inert anodes can be used. A feature of the invention is that a lower operational temperature and electrolyte composition allows for the use of a greater selection of inert anode

15   materials. An advantage of this feature is that the inert anode is not consumed by the electrolytic process. An additional advantage is a significant lowering of costs.

Yet another object of the invention is to provide a low temperature metal production method which uses wetted cathodes. A feature of the invention is that wetted cathodes require only a thin film of molten aluminum on their surface. An

20   advantage of this feature is that fluctuations at the bath aluminum interface resulting from magnetic fields generated in the molten aluminum are minimized, allowing a lower anode-cathode distance that results in a lower cell voltage. Another advantage is that the aluminum film protects the cathode surface from the bath. Yet another advantage is the minimization or prevention of fine aluminum droplets that may become unattached

25   from a cathode that is not wetted, resulting in process inefficiencies due to back reaction at the anode. An additional advantage is further cost savings.

Still another object of the invention is to provide a metal production method which can use vertical or slanted inert anodes, and vertical or slanted wetted cathodes. A feature of this invention is a decrease in the footprint of the electrolytic cell for a given

production rate. An advantage of this feature is easier energy management of the electrolytic process. A smaller electrolytic cell both needs less heat input and has a lesser heat loss due to a smaller surface area and less heat radiation. Since less heat input is required, an additional advantage is that a lower current density (CD) can be

5   used further reducing cell voltage. This feature thus gives additional savings.

Yet another object of the present invention is to provide a method whereby the distance between the electrodes remains constant during the electrolytic process. A feature of the invention is that inert anodes and wetted cathodes are used. An advantage of this feature is that energy savings can be realized through control of the

10   anode-cathode distance.

Still another object of the present invention is to provide a method of alumina electrolysis whereby the generation of greenhouse gases, e.g., carbon dioxide and fluorocarbons, is eliminated. A feature of the invention is that the anodes used are inert. An advantage of this feature is that the only gas generated during the electrolysis of

15   alumina is oxygen (O_2). An additional advantage is that costs are lowered even more due to the elimination of the carbon plant for the production of carbon anodes, and a reduced need for any emission controls.

Briefly, the invention provides an improved electrolyte for the low-temperature electrolysis of alumina (Al_2O_3), the electrolyte comprising alumina, and a mixture of

20   aluminum fluoride (AlF_3) and potassium fluoride (KF).

The invention also provides a method for using inert anodes and wetted cathodes in the electrolytic production of aluminum comprising using the anodes and cathodes in an electrolysis process selected at a temperature selected from between 660^0C and 1000^0C.

25   In addition, the invention provides a method for electrolyzing alumina below 1000^0C, the method comprising supplying an electrolyte containing more than 35 mol% potassium fluoride (KF) and more than 30 mol% aluminum fluoride (AlF_3); injecting alumina with the electrolyte; and subjecting the electrolyte to a voltage.

BRIEF DESCRIPTION OF DRAWINGS

The invention together with the above and other objects and advantages will be best understood from the following detailed description of the preferred embodiment of the invention shown in the accompanying drawing, wherein:

FIG. 1 is a schematic diagram of the potassium fluoride-aluminum fluoride binary system, in accordance with features of the present invention;

FIG. 2 is a schematic diagram of a vertical electrode arrangement design, in accordance with features of the present invention;

FIG. 3 is a schematic diagram of an electrolysis cell for testing electrodes; and

FIG. 4 is a plot of electrolysis cell voltage in volts as a function of time for one 50-hour electrolysis run at a current of 100 A with an aluminum-bronze copper alloy inert anode and two wetted cathodes of TiB_2-C composite in a vertical arrangement, in accordance with features of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

The invention provides a low temperature electrolyte system for the electrolytic production of aluminum metal (Al) that enables the use of inert anodes, wetted cathodes, and/or bi-polar electrodes, in vertical, horizontal, or other configurations. The low temperature electrolyte system is based on the aluminum fluoride (AlF_3) – potassium fluoride (KF) binary system, FIG. 1, and can include additives to change electrolyte properties.

Electrolyte Detail

The phase diagram of the AlF_3-KF system, FIG. 1, shows that the system has a much wider range of low temperature (<800°C) liquid compositions than the aluminum fluoride (AlF_3)-sodium fluoride (NaF) system. At 700°C, the single-phase liquid region extends from about 60 mole (mol)% KF – 40 mol% AlF_3 to about 40 mol% KF – 60 mol% AlF_3. Because of this wide range, the bath composition in an AlF_3-KF based system is easier to control and maintain in the liquid phase in commercial low-temperature aluminum electrolysis than that of an AlF_3-NaF-based low temperature bath which has an eutectic temperature at 698°C and is essentially a single-point

composition (no line or region) of 54 mol% NaF – 46 mol% AlF_3 at 700^0C.

Surprisingly and unexpectedly, the inventors have found that the AlF_3-KF-based system is well-suited for electrolytic production of aluminum at temperatures lower than the operating temperatures for the AlF_3-NaF electrolyte system. The AlF_3-KF-based system has higher alumina solubility compared to the AlF_3-NaF-based system. This allows for easier control of the dissolved alumina content of the bath. The AlF_3-KF-based system has the appropriate density and interfacial energy with aluminum to permit effective separation of bath and aluminum metal product and coalescence of aluminum droplets. The AlF_3-KF-based system has adequate viscosity to allow for efficient mixing of the electrolyte resulting from convection due to rising oxygen gas bubbles from the anode during electrolysis. Viscosity is higher when solid particles such as undissolved alumina are present, and may prevent sufficient mixing of the electrolyte. Further, the higher viscosity may hinder the mobility of gas bubbles evolving from the anode, which can result in a higher cell voltage due to excessive gas bubbles present between the anode and cathode, which would increase the resistance of the cell.

In the AlF_3-KF-based electrolyte, lower bath viscosity is aided by the relatively higher alumina solubility (5 wt.% in AlF_3-KF vs. 2 wt.% in AlF_3-NaF), which allows for electrolysis operation in a   liquid melt.

The inventors have also found that aluminum fluoride-potassium fluoride melt compositions with higher cryolite ratios (moles of KF to moles of AlF_3) have better ionic conductivities. Ionic conductivities in the AlF_3-KF system are improved over those in the AlF_3-NaF system. This is most likely due to the wide range of liquid compositions at lower temperatures. The inventors have found that with AlF_3-KF based electrolytes, potassium ions (K^+), due to their larger size, do not intercalate into cathode materials (enter into the cathode substrate materials' lattices), unlike smaller sodium ions (Na^+) in AlF_3-NaF based electrolytes at higher temperatures.

The AlF_3-KF electrolyte at 700°C can have a KF to AlF_3 mole ratio of from about 1.0 (50 mol% AlF_3 – 50 mol% KF) to 1.5 (40 mol% AlF_3 – 60 mol% KF) and where the amount of alumina dissolved in the electrolyte is sufficient to perform electrolysis, from

about 2 wt.% to 6 wt.%. This alumina solubility eliminates the need for a slurry-cell-type operation to maintain a sufficient amount of alumina dissolved in the melt.

A preferred electrolyte embodiment is a KF to AlF_3 mole ratio of about 1.3 (43 mol% AlF_3 – 57 mol% KF) and an alumina concentration of from about 4 wt.% to 5 wt.%. These concentrations improve the electrolysis process by lowering cell voltage. This embodiment is near the liquidus line associated with K_3AlF_6 in FIG. 1. Conductivity of the bath is strongly dependant on the K^+ ion concentration. Thus, baths with higher KF level generally result in a lower cell voltage.

Inasmuch as aluminum metal is being produced at the cathode, the concentration of KF in the near-cathode region can be higher than in the bulk bath during electrolysis. If the bulk bath composition is too near the liquidus line, solid K_3AlF_6 can precipitate on the cathode, decreasing the effective surface area available for electrolysis and increasing cell voltage. Additionally, the precipitate can result in incomplete wetting of a wettable cathode, causing processing inefficiencies, as described *infra*. Thus, the preferred embodiment of the bulk electrolyte composition is given by a KF to AlF_3 mole ratio of about 1.3 rather than 1.5, which is at the liquidus line at 700°C.

Higher temperature improves electrical conductivity and increases the composition range of the liquid, so the temperature of the electrolyte can be higher than 700°C for improved cell operation. The electrolyte can be used at temperatures as high as 1000°C. In such a case, the optimum electrolyte composition will be slightly richer in KF to maintain the optimum composition within about 2 mol% from the liquidus line, further improving the electrical conductivity. Although higher temperatures can lead to higher electrolyte conductivities and lower cell voltages, lower temperatures are less corrosive and enable the use of a larger selection of inert anode materials. The inventors found temperatures of about 700°C to be optimal and thus one preferred embodiment of operation.

Additives can improve or alter the AlF_3-KF electrolyte system properties. One such additive can be NaF, which can be added to the electrolyte or allowed to build up in the electrolyte due to the residual sodium ion (Na^+) level that can be present in the alumina feed to the cell, if the cell is used continually for long periods of time. This

residual NaF can result from the use of sodium hydroxide (NaOH) in the Bayer process for the production of alumina feed.

An increase in NaF in the electrolyte can have detrimental effects on cell performance. At elevated levels of NaF in the electrolyte, a solid deposit can form intermittently on the cathode and cause inefficiencies in the cell, as well as increasing the impurity level of the aluminum metal product.

The inventors have found that small additions of NaF (> 2 wt%) cause detrimental cell operations at both the cathode and anode. The presence of a small amount of Na^+ cations in the bulk electrolyte is magnified in the near-cathode region during electrolysis. During electrolysis, the majority of the electrical current through the cell electrolyte is carried by the cations (Na^+ and K^+) because of their smaller size and greater mobility compared to the anions in the electrolyte. Because Na^+ cations are smaller and more mobile than K^+, Na^+ cations tend to concentrate near the negatively-charged cathode surface. The increase in local NaF/KF ratio in the near-cathode region changes the local electrolyte composition, which decreases the alumina solubility in the region, and causes alumina and/or cryolite-type compounds to precipitate on the cathode as an intermittent grayish film. The inventors have observed this film.

The presence of this film on the cathode surface disrupts cell operation by preventing aluminum from wetting the cathode and disrupting aluminum metal coalescence. The aluminum metal which forms on the cathode tends to become dispersed in electrolyte as fine droplets of molten aluminum that are swept up by convection currents in the bath. The aluminum droplets can even come in contact with the anode, disrupting the anode surface film and accelerate the anode wear rate. Other cations, including alkali or alkaline earth cations, can also play a role as minor additives to this base electrolyte to modify the liquidus region or physical properties of the electrolyte.

In addition to the detrimental effects caused at the cathode that could also effect the anode, the presence of Na^+ in the electrolyte can have a detrimental effect which can contribute to a higher anode wear rate. Sodium ion can cause redistribution of anion moieties in the electrolyte and alter the effect anion moieties have on anode wear. The primary oxygen-containing anion moieties in the $KF-AlF_3-Al_2O_3$ electrolyte are most

likely oxyhexafluorodialuminate ion ($Al_2OF_6^{2-}$) and dioxytetrafluorodialuminate ion ($Al_2O_2F_4^{2-}$). During electrolysis, $Al_2O_2F_4^{2-}$ is readily oxidized to $Al_2OF_6^{2-}$ liberating oxygen gas, while $Al_2OF_6^{2-}$ is not significantly oxidized. Thus, the total concentration of both oxygen-containing anions in the electrolyte at the anode surface does not change significantly. This is significant if the anode surface is an oxide film or oxygen-containing species, as it most likely is in most inert anode formulations. The driving force to dissolve the oxide film or oxygen-containing species on the anode surface is minimal because of the presence of oxygen-containing anions in the electrolyte at the anode surface. Control of the electrolyte bath composition in the AlF_3-KF system is more flexible than in the AlF_3-NaF system due to only small losses of $KAlF_4$ from the electrolyte melt.

In NaF-AlF_3-Al_2O_3 electrolytes the ratio $Al_2OF_6^{2-}$ anions to $Al_2O_2F_4^{2-}$ anions is significantly greater than in KF-AlF_3-Al_2O_3 electrolytes. During electrolysis, the primary oxidation reaction at the anode is likely the conversion of $Al_2OF_6^{2-}$ to AlF_4^- liberating oxygen gas. The result is a lower number of oxygen containing species at the anode surface, and a subsequent higher driving force to dissolve the oxide film on the anode and increasing the anode wear rate. Therefore, there appears to be a limit to which NaF can be added to a KF-AlF_3-Al_2O_3 electrolyte without significantly increasing the anode wear rate. The limit is related to the concentration of $Al_2O_2F_4^{2-}$ species in the melt. The inventors found this limit is less than 2 wt.% NaF. Above this concentration of NaF in the electrolyte, excessive anode wear can occur. The same effect exists for other additives such as lithium fluoride (LiF).

An electrolyte-cleansing operation can be used either *in situ* or *ex situ* of the cell, and the detrimental moiety can be removed by a variety of means, e.g., collection by zeolite-like or porous carbon structures. In the alternative, the detrimental moiety can be reduced in the electrolyte by altering upstream processing, i.e., using KOH in the aforementioned Bayer process to reduce the sodium content in the alumina feed.

Electrode Detail

Due to the lower temperature of the AlF_3-KF based electrolyte system discussed *supra*, the invented low temperature electrolyte system uses low-cost metal materials in the form of inert anodes and wettable cathodes. As such, commercially-available

metals and metal alloys can be used as inert anodes in the instant invention. Composite materials can be used for wettable cathodes.

The use of inert anodes allows for the distance between anode and cathode to be constant during the electrolysis of alumina. This feature provides an electrically stable electrolysis environment.

In addition to inert anodes and wetted cathodes, the invented electrolyte system works works well with other electrodes, including conventional carbon anodes and carbon cathodes.

1. Anodes

The anode is comprised of a material selected from the group consisting of metals, metal alloys, metal oxides, and cermets. The alloys can be aluminum-bronze alloys, i.e., alloys that are primarily copper and have significant amount of added aluminum (1 to 20 wt.%). Commercially available aluminum-bronze alloys (including, but not limited to, Unified Numbering System (UNS) numbers C60800 to C60210, and C95200 to C95900) appear well suited for use as inert anodes. For example, alloy C63000 (specifications: 9.0 to 11.0 wt.% Al, 4.0 to 5.5 wt.% Ni, 2.0 to 4.0 wt.% Fe, 1.5 wt.% Mn, 0.30 wt.% Zn, 0.25 wt.% Si, 0.20 wt.% Sn) performed well, and thus is a preferred formulation for an inert anode.

Preferable anodes are metal monoliths which have a stable oxygen-containing film that forms during electrolysis and does not contribute significantly to the cell operating voltage. Typically, the anodes with oxide or oxygen-containing films have a polarization voltage of less than 0.5 volts (V) at a current surface density of 0.8 amperes per square centimeter (A/cm^2).

Metallic anodes have other advantages which include improved electrical conductivity through the anode, improved resistance to thermal shock, and improved toughness and ductility for easier fabrication, handling, and installation.

Commercially-available copper-based alloys perform satisfactorily, particularly the aluminum-bronze copper alloys such as UNS C63000. The impurity levels of the aluminum metal product formed using UNS C63000 as the anode were 0.09 wt % Cu, 0.03 wt % Fe and <0.01 wt % Ni in a 50-hour (hr) electrolysis test (*infra*) at a total current of 100 A using a commercial copper alloy as the anode.

2. Cathodes

The cathode is made of a material compatible with the environs associated with alumina electrolysis. Generally, suitable material is that wetted by aluminum. Appropriate cathode substrate material includes that selected from the group consisting

5   of metal borides, metal boride-carbon composites, metal boride-containing coatings on substrates, graphite (C), molybdenum (Mo), and tungsten (W). The metal borides include, but are not limited to, those of titanium (Ti) and zirconium (Zr). Other materials which can be wetted by aluminum can be used as cathodes.

Molten aluminum wets well the TiB_2-C composite. Wettable cathodes decrease

10   the cathodic over potential during electrolysis, compared to non-wetted cathodes, and allow for a lower anode-to-cathode distance during electrolysis, further decreasing operating voltage. Wetted cathodes also promote coalescence of the molten aluminum product thereby improving the efficiency of the process by minimizing back reactions. The use of wetted cathodes and inert anodes is enabled by the low-temperature

15   electrolyte and allows for the arrangement of anode and cathode in a vertical position.

A vertical arrangement allows metal that forms on the cathode to drip off the bottom of the cathode and collect at the bottom of the cell. In addition, the vertical configuration lowers the anode-cathode distance and allows for a smaller cell footprint or size, leading to lower heat input requirements. Lower heat input makes possible

20   lower current densities which further adds to cell efficiency. In cells with horizontally-arranged electrodes, a lesser anode-cathode distance aids in minimizing process inefficiencies due to fluctuations at the bath-aluminum interface resulting from magnetic fields generated in the aluminum metal pad during electrolysis.

Cathodes made of TiB_2-C composite are wetted by the aluminum at $700^{0}C$ and

25   perform well as cathodes in the AlF_3 - KF electrolyte. Other materials wetted by aluminum will also perform well.

FIG. 2 *infra* serves to illustrate the concept of a cell with a vertical electrode design. The number of electrodes shown is one possible illustration and embodiment.

Electrolytic cell configuration

30   The orientation of the inert anodes and wetted cathodes in the cell can be vertical, slanted, or horizontal. A vertical design using the sequence anode 12 –

cathode 14 – cathode 14 – anode 12 - cathode 14 - cathode 14 - anode 12 is depicted in FIG. 2 as numeral 10. In this sequence, electrolysis occurs between the anode 12 and cathode 14, but not between the two adjacent cathodes 14. Oxygen evolving during electrolysis sweeps the electrolyte to the top of the cell. The electrolyte returns to the bottom of the cell through the cathode-cathode chambers 18.

Thus, electrolyte recirculation paths are established in the spacing regions between adjacent cathodes 14. This arrangement promotes convection currents through the cell and maintains a more uniform electrolyte composition. The spacing between the chambers can be optimized for electrolyte flow and velocity, taking into account evolving oxygen gas. Many electrode arrangements are possible that include regions in the cell where electrolysis does not occur and recirculation paths are established.

The lower operating temperature of the invented AlF_3-KF electrolyte system allows for bipolar plates to be used in multi-polar cells. The cathode materials described *supra* can be used to coat one side of an inert anode to create a bipolar electrode for use in multipolar electrolytic cells. For example, bipolar electrodes can comprise an aluminum bronze inert anode coated with TiB_2 on a first side. At the lower operating temperature of the invented AlF_3-KF electrolyte system, TiB_2 can also be used directly as the plate material in bipolar cells. In a cell configured with bipolar plates, the electrode arrangement can be such that electrolyte recirculation paths are established.

The following example is simply to illustrate the testing and use of the new electrolyte and electrodes of the instant invention and to demonstrate their effectiveness.

FIG. 3 *infra* serves only to illustrate the general aspects of an electrolytic cell and the cell's components.

Example

One electrolysis run was carried out for a period of 50 hours (hrs) at a current of 100 amperes (A). A schematic diagram of the basic form of the experimental cell is depicted in FIG. 3 as numeral 30. The cell's 30 components are contained in a sintered alumina crucible 32, which is depicted as generally cylindrical in shape. Alumina is fed into the cell 30 via a sintered alumina tube 34, which has a first end 36 protruding from

the cell, and a second end 38 protruding within the confines 40 of the cell. The temperature is monitored with a platinum (Pt)-Pt-10 % rhodium (Rh) thermocouple 42 housed in a closed-end alumina tube 44. A first end 46 of the thermocouple 42 terminates with pair of electrical leads 48, while a second end 50 of the thermocouple 42, swathed in the alumina tube 44, is immersed in the electrolyte 52 (represented by the dashed lines).

A stainless steel rod 54 extending generally parallel with the longitudinal axis of the crucible, serves as a current lead for the anode 56. Generally, the anode is placed in a concentric position within the cell for optimized results. The faces of the two cathodes 58 are parallel to the faces of the anode 56. The cathodes 58 have stainless steel current leads 60. Sintered alumina sheaths 62 protect and electrically insulate the stainless steel rod 54, and the stainless steel current leads 60. The aluminum fluoride-potassium fluoride melt 52 is contained within the cell 30, and typically confined at one end of the cell via gravity. The stainless steel current leads 60, the alumina feeding tube 34, and the thermocouple 42 relative positions are secured by holes in the top of the cell, all of which, as mentioned *supra*, extend generally parallel to the longitudinal axis of the crucible 32.

Runs were carried out under an argon (Ar) atmosphere. The argon gas flow was kept at 1.13 Liters per minute (L/min). An oxygen sensor was mounted on the outlet gas path to measure the amount of oxygen generated on the alloy anodes.

The basic cell design (FIG. 3) as used for the 50-hr, 100 A run, employed a parallel vertical plate arrangement. Three plate electrodes were employed comprising a central anode plate between two cathode plates. The size of each electrode plate was approximately 133 millimeters (mm) wide, 85 mm high, and 12 mm thick. The anode was made of aluminum-bronze (alloy C63000, composition specifications given *supra*), and the cathodes were made of TiB_2-C composite. The anode-cathode distance was 2.3 cm. The initial electrolyte composition was 50 wt.% AlF_3, 45 wt.% KF, and 5 wt. %Al_2O_3. Alumina was fed continuously to the cell during electrolysis. The electrolysis test was performed at 700°C and the anode current density was maintained at 0.44 A/cm^2 for the duration of the 50-hr test.

FIG. 4 depicts a plot of electrolysis cell voltage in volts as a function of time for this run. The voltage remains fairly constant at a current of 100 A for a period of 50 hr. A significant amount of aluminum product corresponding to a current efficiency of 85% was recovered at the conclusion of the test run. Subsequent analysis indicated impurity levels of 0.09 wt.% Cu, 0.03 wt.% Fe and <0.01 wt % Ni. Anode wear was not detected, although a 200-300 micrometer (μm) thick oxide film was found on the surface of the anode.

While the invention has been described with reference to details of the illustrated embodiment, these details are not intended to limit the scope of the invention as defined in the appended claims.